PB86-244217

Design of Fixed-Beds to Remove Multicomponent Mixtures of Volatile Organic Chemicals

Michigan Technological Univ., Houghton

Prepared for

Environmental Protection Agency, Cincinnati, OH

1985

U.S. Department of Commerce
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1. REPORT NO.	2.	3.
EPA/600/D-86/205		PB86-244217

4. TITLE AND SUBTITLE	5. REPORT DATE
DESIGN OF FIXED-BEDS TO REMOVE MULTICOMPONENT MIXTURES OF VOLATILE ORGANIC CHEMICALS	1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
J.C. Crittenden, G. Friedman, D.W. Hand, J. Berrigan, and T. Speth	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Michigan Technological University Houghton, Michigan 499310	
	11. CONTRACT/GRANT NO.
	CR 811150-01-0
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Water Engineering Research Laboratory- Cincinnati, OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	Published Paper
	14. SPONSORING AGENCY CODE
	EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer, B.W. Lykins; In: Proceedings; AWWA, 1985 Annual Conference, Washington, D.C., June 23-27, 1985, pp. 1327-1346.

16. ABSTRACT

Laboratory bench-scale experiments determined that the ideal adsorbed solution theory (IAST) was adequate to predict multicomponent competitive interactions of adsorbates from single solute isotherm experiments. A correlation (developed by Williamson et al.) for the film transfer coefficient was sufficient to predict the these coefficients for the VOC's. A correlation was also developed to estimate the surface diffusivity. The homogeneous surface diffusion model (HSDM), which incorporates IAST and the mass transfer correlations, can predict the multicomponent breakthough of VOC's.

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	22
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

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DESIGN OF FIXED-BEDS TO REMOVE MULTICOMPONENT MIXTURES OF VOLATILE ORGANIC CHEMICALS

EPA/600/D-86/205

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I. Objectives:

1. Laboratory bench scale experiments were to be conducted to determine whether ideal adsorbed solution theory (IAST) can predict multicomponent competitive interactions from single solute isotherm experiments. Bench scale experiments were to be used to determine the film transfer and surface diffusion coefficients which are required in a predictive mathematical model.

2. A mathematical model was to be developed and verified by comparing it to the performance of granular activated carbon (GAC) pilot plant data.

3. The utility of the model in the proper design of fixed-bed adsorbers was to be demonstrated.

II. Predictive Thermodynamic and Mass Transfer Models:

In order to make predictive calculations with the homogeneous surface diffusion model (HSDM), these four parameters must be determined for each adsorbing component: (a) Freundlich capacity parameter, K, (b) Freundlich intensity parameter, 1/n, (c) film transfer coefficient, k_f, and (d) surface diffusion coefficient D_s. In this section, it was demonstrated that the mass transfer parameters of the HSDM may be determined from correlations and that multicomponent interactions may be predicted from ideal adsorbed solution theory (IAST). In addition, this model was verified by demonstrating that it could predict several field and laboratory fixed-bed adsorbers.

A. Ideal Adsorbed Solution Theory

IAST may be used to predict multicomponent competitive interaction between adsorbates. IAST requires the Freundlich isotherm parameters, K and 1/n, of the individual components and their initial concentrations as shown in this equation.

AWWA 1985 Annual Conference Proceedings, "Managing a Priceless Resource"; Washington, DC, June 23-27, 1985 (pp. 1327-1346)

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$$C_i = \frac{q_i}{\sum_{j=1}^{N} q_j} \left[\frac{\sum_{j=1}^{N} n_j q_j}{n_i K_i} \right]^{n_i} \qquad (1)$$

The mixture which is reported in Figure 1 was for water that was obtained from Well No. 4 at Wausau, Wisconsin and Table 1 displays the components which were present and their respective concentrations.

B. Diffusion Mechanisms which Are Present in the Adsorption Rate.

Figure 2 depicts the mechanisms which are present in the adsorption process. Since the pore diffusion contribution to the solute flux is usually negligible, only the film transfer coefficient and surface diffusivity need to be determined in order to use the homogeneous surface diffusion model (HSDM).

As shown in Figure 3, the film transfer coefficient may be calculated with sufficient precision using the following equation by Williamson et al.

$$Sh = \frac{k_f\ 2R}{D_L} = 2.4\ \varepsilon\ Re^{0.34}\ Sc^{0.42} \qquad (2)$$

in which, k_f is the film transfer coefficient, D_L is the liquid-phase diffusivity, ε is the bed void fraction, R is the GAC particle radius, Sc is the Schmidt number, and Re is the Reynolds number.

$$Re = \frac{2R\ v_s\ \rho_L}{\mu\ \varepsilon} \qquad (3)$$

$$Sc = \frac{\mu}{\rho_L\ D_L} \qquad (4)$$

in which, μ is the viscosity of the fluid and ρ_L is the fluid density. The liquid diffusivity, D_L, may be determined from this correlation (Hayduk and Laudie):

$$D_L = \frac{13.26 \times 10^{-5}}{\mu^{1.14}\ V_b^{0.589}} \qquad (5)$$

in which, V_b is the molal volume of the adsorbate at its boiling point.

Based on data which was collected for volatile organic compounds (VOCs) and data which was presented in the literature the following correlation was developed for the calculation of the surface diffusion coefficient.

$$D_s = PDFC \cdot PSDFR \qquad (6)$$

$$PDFC = \frac{\varepsilon_p\ D_L\ C_o}{\varepsilon_a\ K\ C_o^{1/n}} \qquad (7)$$

in which, the pore surface diffusion flux ratio (PSDFR) is the ratio of the surface diffusion flux to the pore diffusion flux contribution (PDFC) which is evaluated at the influent concentration. Since the PDFC may be calculated from the chemical and physical properties of the adsorbates and adsorbents, the PSDFR is the correlating parameter.

Figure 4 displays a plot of the calculated PDFC as compared to the observed surface diffusivities. The slope of this line is equal to the PSDFR which is equal to 6.58. As shown in Figure 4, the correlation provides a satisfactory description of the VOC and some substituted aromatic data. The correlation coefficient was 0.89.

In cases where the pore diffusion flux was included (in the pore surface diffusion model [PSDM] calculations) the pore diffusion coefficient, D_p was calculated according to the following equation:

$$D_p = D_L\ \varepsilon_p \qquad (8)$$

C. Verification of the HSDM Using the Correlations for the Film Transfer and Surface Diffusion Coefficients.

The following figures demonstrate that the HSDM and the simple correlations which are presented above may be used to predict adsorber performance with sufficient precision to design a fixed-bed adsorption system.

III. Utilization of Models for Design of Fixed-Bed Adsorption Systems.

Once it was demonstrated that the HSDM predicted multicomponent data with sufficient precision, it may be used to select the appropriate fixed bed process. In addition to the HSDM, the equilibrium column model (ECM) was developed which assumes local equilibrium exists throughout the fixed bed. The ECM may be used to determine the elution order of individual components in a multicomponent mixture, the maximum number of volumes of water that a bed may treat and the highest overshoot concentration which would be observed in a fixed-bed adsorber.

To demonstrate the utility of the ECM and HSDM, calculations were performed for the components which were present in Wausau Well No. 4 and the results are presented in Table 2.

From the ECM, it was found that the largest number of bed volumes of water that may treated and the highest overshoot concentrations that would be observed are those reported in Table 2. Using the HSDM, it was demonstrated that a six-component model was not needed to predict the effluent concentration history profiles of the first three components which leave the fixed-bed adsorber. If the the overshoot concentrations which were observed from the ECM were used in the HSDM, only a three-component model was needed to predict the breakthrough of the first three components from the fixed-bed. It was also demonstrated that only a single-component model was needed to predict the first component that leaves fixed-bed adsorber, if its respective overshoot concentration from the ECM was used as the influent concentration. Obviously, this greatly simplifies the computational effort of the HSDM. Currently, it takes about 45 minutes of core time on the IBM 4341 minicomputer to calculate a six-component breakthrough profile using the HSDM and about 8 minutes to run a single-component HSDM on the IBM-PC with a 8087 coprocessor.

The utilization of the models for design is illustrated in Figures 10-11. The maximum number of bed volumes that may treated as a single solute and in a multicomponent mixture is plotted at the top of each figure and was calculated using the ECM. The HSDM was used to calculate the number of bed volumes which can be treated until .01 of the influent concentration breaks through the adsorber. Since there is some deviation from the correlation for the surface diffusivity, these calculations were repeated for several values of the correlating parameter the PSDFR. As shown in Figures 10-11, this correlating parameter has little impact on the number of bed volumes that a fixed bed may treat before it exceeds a treatment object of .01 of the influent concentration. These figures also demonstrate that more bed volumes of water may be treated as the the EBCT is increased and that two adsorber operated in series does increase the number of bed volumes that may treated. These Figures may be used in combination with cost information to select the cheapest fixed-bed process.

One difficulty that has received little attention is the impact of backwashing. By using anaerobic groundwater and a low hydraulic loading such a 5 m/hour, we have demonstrated that our pilot plant has not needed to be backwashed for 10 months of operation. The Figure 12 demonstrates the impact of backwashing using the HSDM. Obviously, if the fixed bed is backwashed every 3 days the bed life is greatly diminished. These calculations assume the worst case and that is the bed is completely mixed after each backwashing. Although, no data was collected to verify this effect, we did observe that a full scale unit that was treating Well No. 6 in Wausau and which was backwashed about once a week did not last nearly as long as it should have based on the estimated capacity of the carbon.

IV. Case Study - Analysis of Wausau Pilot Plant Data

A GAC pilot plant which is shown in Figure 13 was conducted on Well No. 4 in Wausau, Wisconsin for 10 months for various EBCTs and the results shown in Figures 14-15 were observed in the field. Figures 14 - 15 demonstrate that the number of bed volumes that may be treated increased as the EBCT increases. This data may be examined to evaluate the tradeoff between the size of the fixed-bed adsorber and the increased bed life. Obviously, this data is sufficient to design to the fixed-bed process for the conditions which were observed but how would the the full scale plant behave if the conditions were different? Once the HSDM has been shown to predict this data, we can use the HSDM to answer this question. As we gain more confidence in the predictive capability of the HSDM, we may be able to avoid the time and expense of such a pilot plant.

V. Conclusions

1. Ideal adsorbed solution theory (IAST) was adequate to predict the multicomponent competitive interactions of adsorbates from single solute isotherm data.

2. A correlation which was developed by Williamson et al. for the film transfer coefficient was sufficient to predict the film transfer coefficients for the VOCs.

3. A correlation was developed for the estimation of the surface diffusivity.

4. The homogeneous surface diffusion model (HSDM) which incorporates IAST and the mass transfer correlations can predict the multicomponent breakthrough of VOCs.

5. The HSDM and the equilibrium column model (ECM) are useful in design of fixed-bed adsorbers that treat multicomponent mixtures.

VI. Acknowledgments

This research is based upon work supported by the National Science Foundation under grant CEE-8300213 from the Environmental and Water Quality Engineering Program, by the EPA under cooperative agreement from the Municipal Environmental Research Laboratory (No. CR811150-01-0) and by the Water and Waste Management Programs at Michigan Technological University. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the National Science Foundation, Environmental Protection Agency or the Water and Waste Management Programs.

Table 1. Components which Were Present in Wausau Well No. 4 Water on March 2, 1985.

Component	Concentration
cis,1,2-Dichloroethene	61.4 µg/L
Trichloroethene	30.2 µg/L
Tetrachloroethene	24.4 µg/L
Toluene	14.5 µg/L
Ethyl Benzene	3.0 µg/L
m-Xylene	3.6 µg/L
o,p-Xylene	9.2 µg/L
Total Organic Carbon	7.66 mg/L

Table 2. Maximum number of Bed Volumes that May Be Treated and the Highest Overshoot Concentrations that May Be Observed Using the Equilibrium Column Model and the Components and Concentrations.

Component	Influent Concentration in µg/L	Maximum No. Of Bed Volumes Treated	Highest Overshoot Concentration in µg/L
cis,1,2-Dichloroethene	100.	17,300.	125.
Trichloroethene	100.	70,000.	215.
Toluene	100.	100,996.	137.
Ethyl Benzene	20.	112,000.	24.
Tetrachloroethene	100.	298,000.	126.
Xylenes	20.	1,076,000.	20.

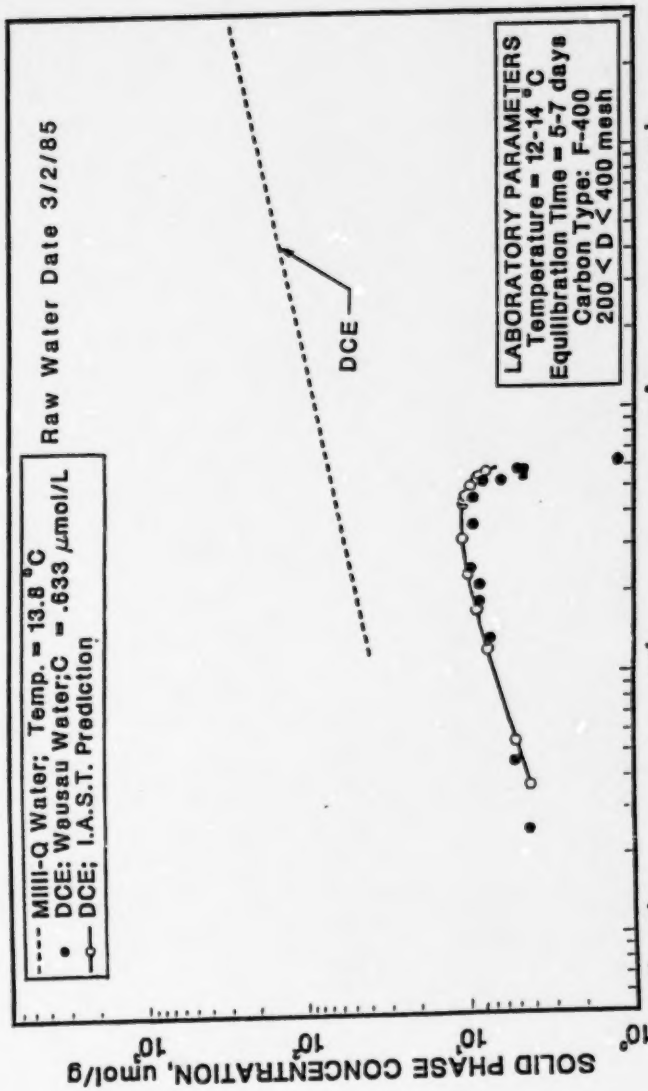


Figure 1. Ideal Adsorbed Solution Theory Prediction as Compared to Equilibrium Isotherm Data for DCE. IAST prediction assumes that only the VOCs cause competitive adsorption interactions.

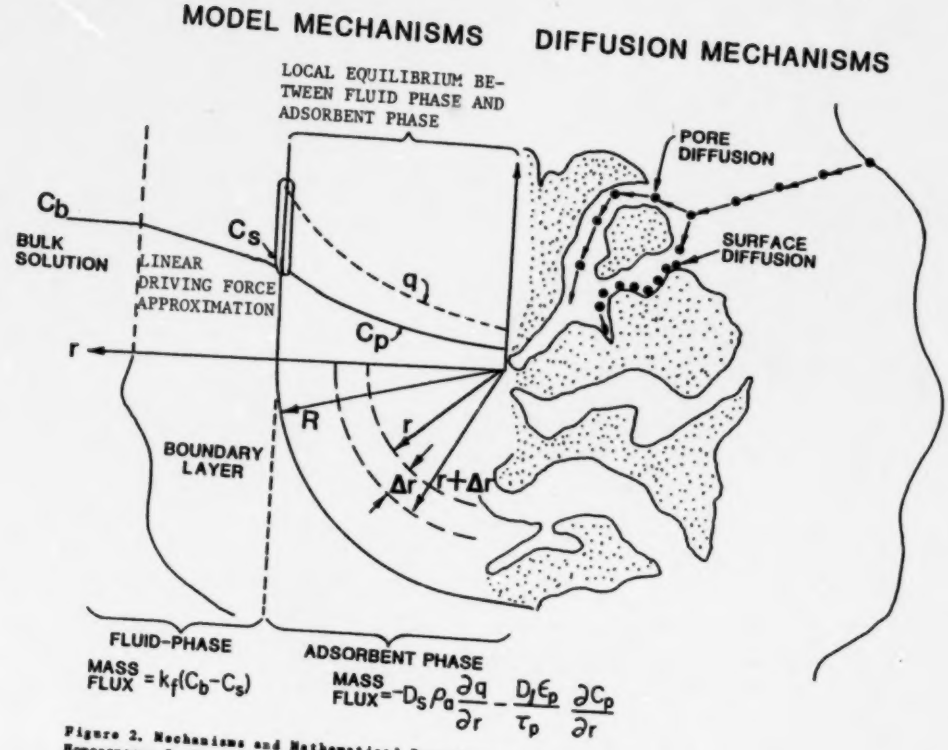


Figure 2. Mechanisms and Mathematical Descriptions which Are Used in the Homogeneous Surface Diffusion Model.

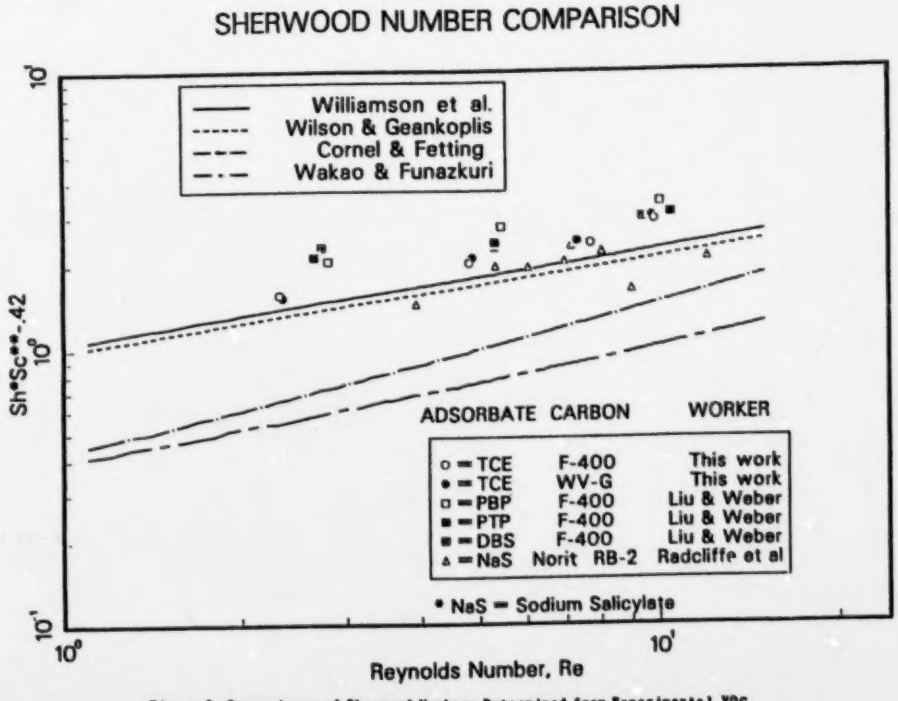

SHERWOOD NUMBER COMPARISON
Williamson et al.
Wilson & Geankoplis
Cornel & Fetting
Wakao & Funazkuri
Sh*Sc**-.42
Reynolds Number, Re
ADSORBATE CARBON WORKER
○ = TCE F-400 This work
● = TCE WV-G This work
□ = PBP F-400 Liu & Weber
■ = PTP F-400 Liu & Weber
■ = DBS F-400 Liu & Weber
△ = NaS Norit RB-2 Radcliffe et al
* NaS = Sodium Salicylate

Figure 3. Comparisons of Sherwood Numbers Determined from Experimental VOC Data to Those Calculated from Various Literature Correlations.

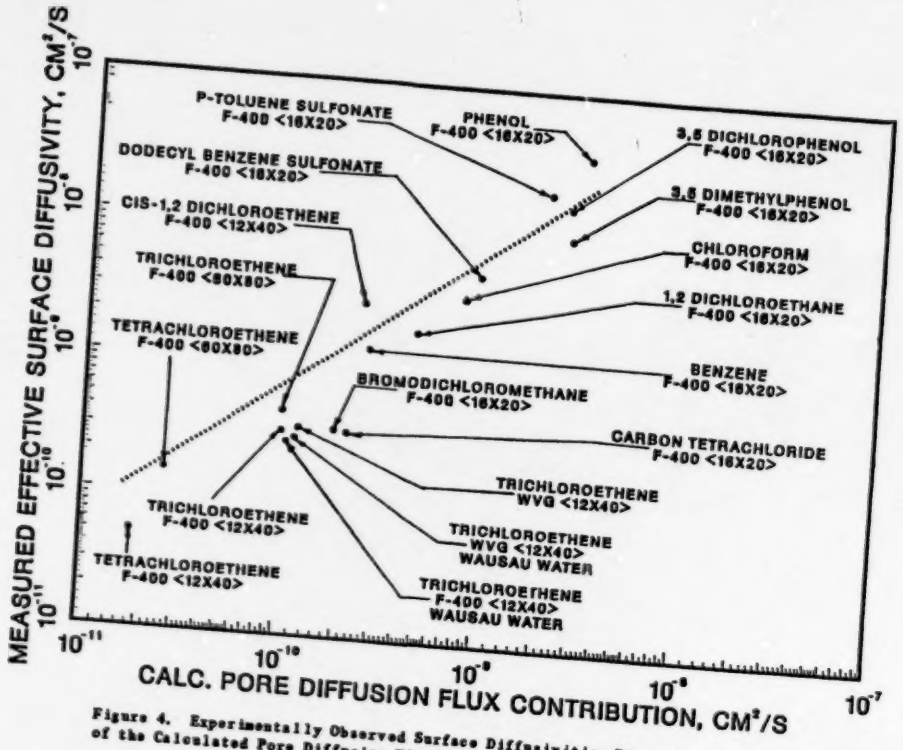


Figure 4. Experimentally Observed Surface Diffusivities Plotted as a Function of the Calculated Pore Diffusion Flux Contribution.

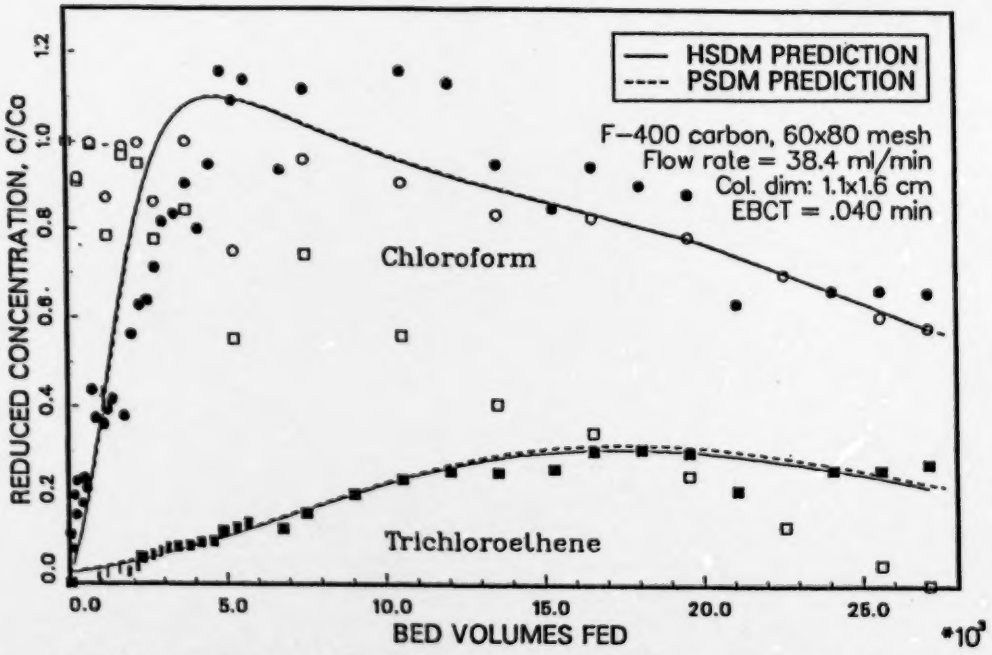


Figure 5. HSDM and PSDM Predictions of a Two-Component Laboratory Column Study. The Open Symbols Are the Influent Concentrations and the Solid Symbols are the Effluent Data. The Trichloroethene and Chloroform Concentrations Were Normalized by Dividing Them by Their Initial Influent Concentrations of 26.3 and 39.8 μM/L, Respectively.

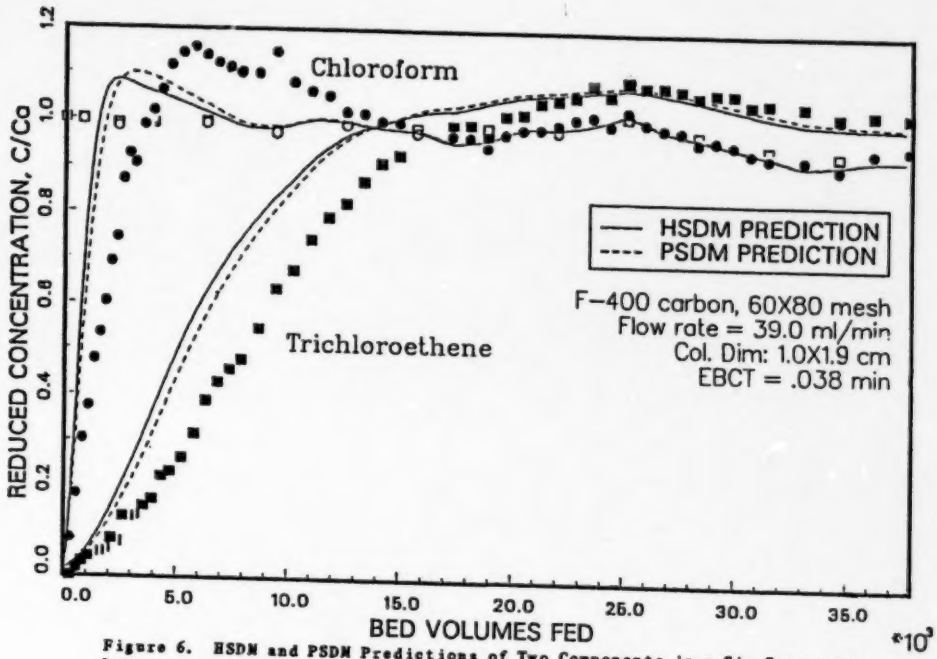


Figure 6. HSDM and PSDM Predictions of Two Components in a Six-Component Laboratory Column Study. The components which were present are Chloroform, Chlorodibromomethane, 1,2-Dibromoethane, Bromoform, Trichloroethene, and Tetrachloroethene. The Open Symbols Are the Influent Concentrations and the Solid Symbols are the Effluent Data. The Trichloroethene and Chloroform Concentrations Were Normalized by Dividing Them by Their Initial Influent Concentrations of 29.2 and 22.97 μM/L, respectively.

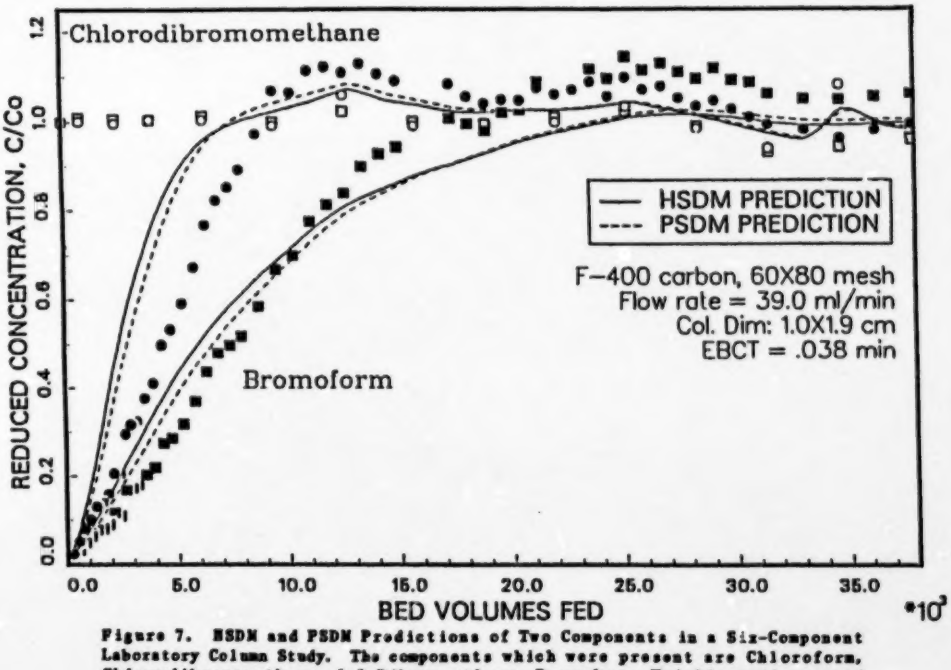


Figure 7. HSDM and PSDM Predictions of Two Components in a Six-Component Laboratory Column Study. The components which were present are Chloroform, Chlorodibromomethane, 1,2-Dibromoethane, Bromoform, Trichloroethene, and Tetrachloroethene. The Open Symbols Are the Influent Concentrations and the Solid Symbols are the Effluent Data. The Chlorodibromomethane and Bromoform Concentrations Were Normalized by Dividing Them by Their Initial Influent Concentrations of 25.6 and 18.8 μM/L, respectively.

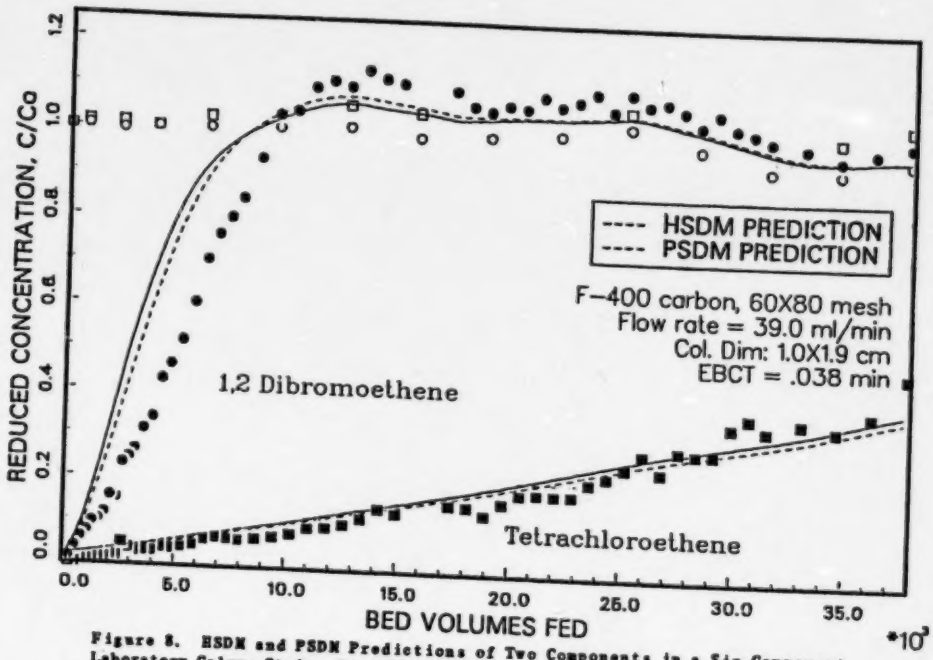


Figure 8. HSDM and PSDM Predictions of Two Components in a Six-Component Laboratory Column Study. The components which were present are Chloroform, Chlorodibromomethane, 1,2-Dibromoethane, Bromoform, Trichloroethene, and Tetrachloroethene. The Open Symbols Are the Influent Concentrations and the Solid Symbols are the Effluent Data. The 1,2-Dibromoethane and Tetrachloroethene Concentrations Were Normalized by Dividing Them by Their Initial Influent Concentrations of 25.6 and 18.8 μM/L, respectively.

Figure 9 - Not included

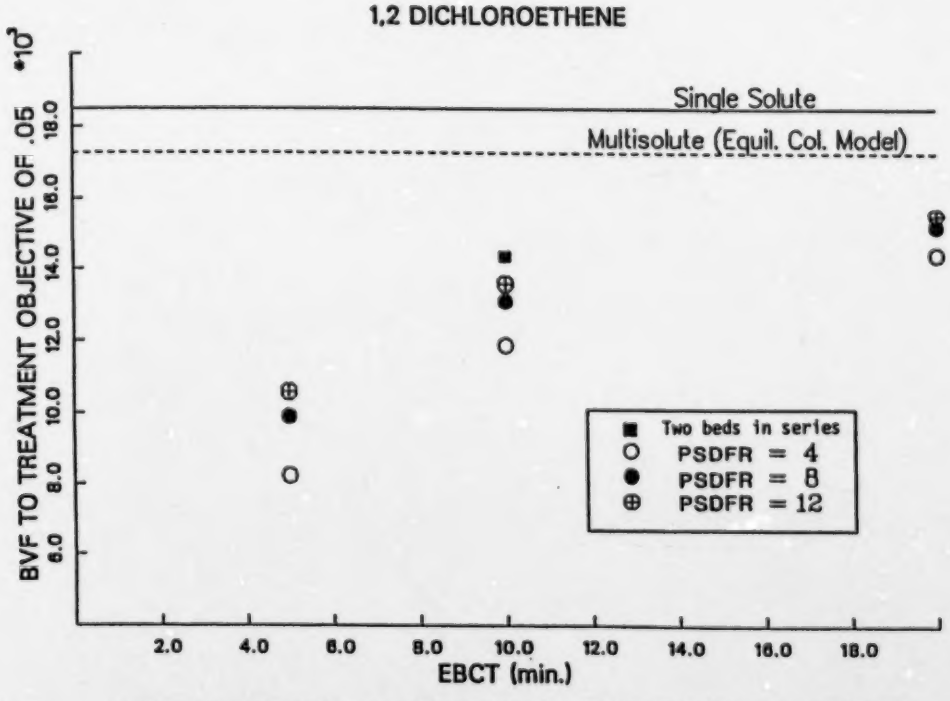


Figure 10. The Number of Bed Volumes that May Be Treated for a Treatment Objective of 0.01 of the Influent Concentration for cis 1,2-Dichloroethene in a Single Adsorber and Two Adsorbers in Series Using the HSDM.

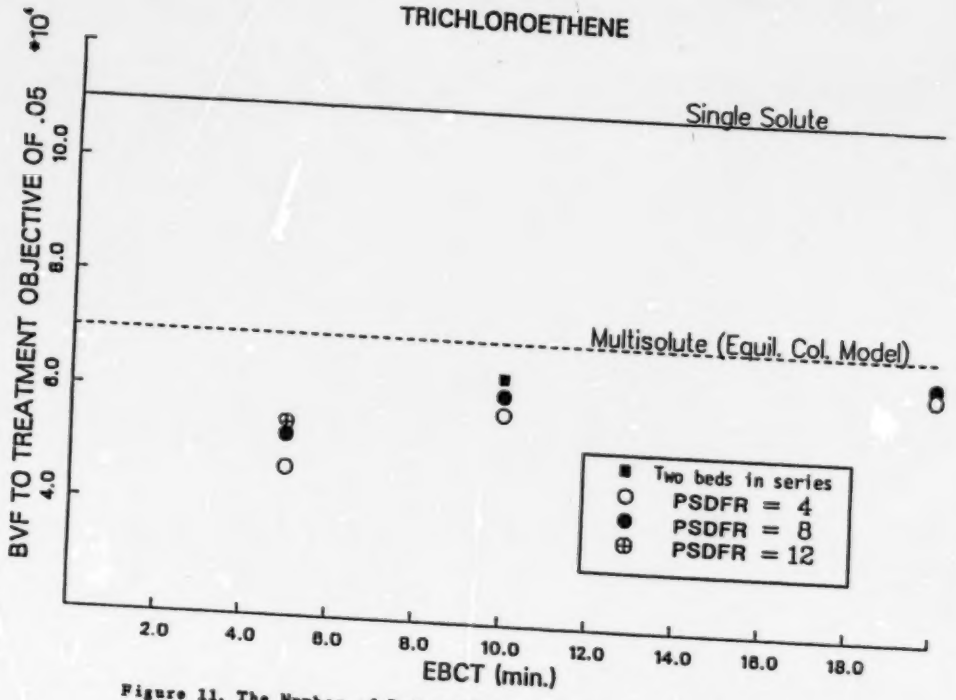


Figure 11. The Number of Bed Volumes that May Be Treated for a Treatment Objective of 0.01 of the Influent Concentration for Trichloroethene in a Single Adsorber and Two Adsorbers in Series Using the HSDM.

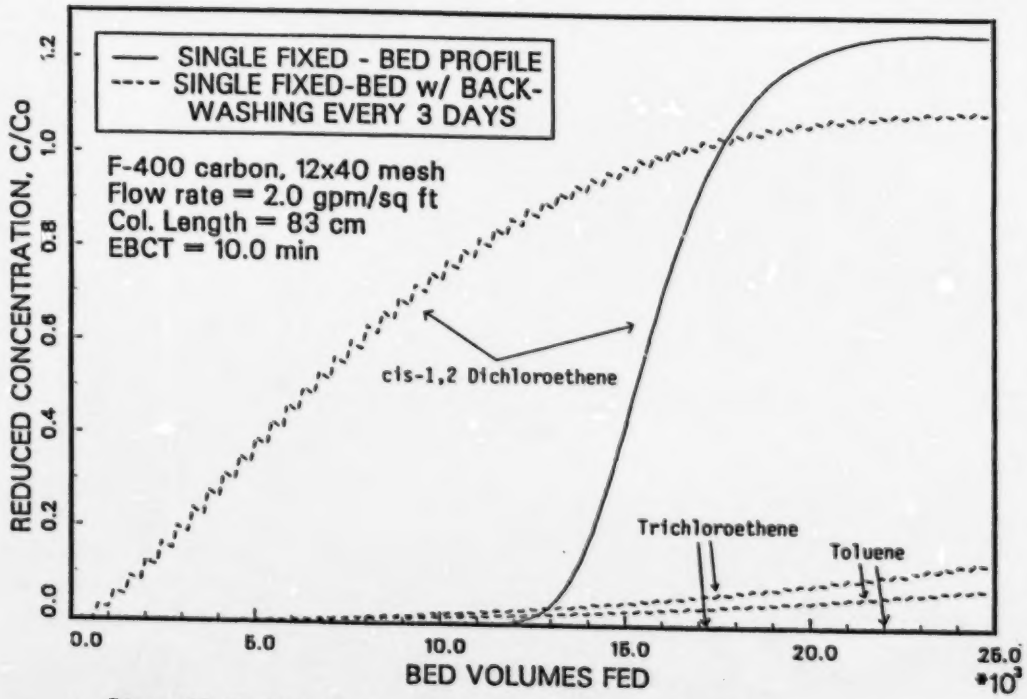


Figure 12. Predicted cis 1,2-Dichloroethene, Trichloroethene, and Toluene Breakthrough Profiles Using the HSDM for a Single Adsorber and a Single Adsorber which Is Backwashed Every 3 Days.

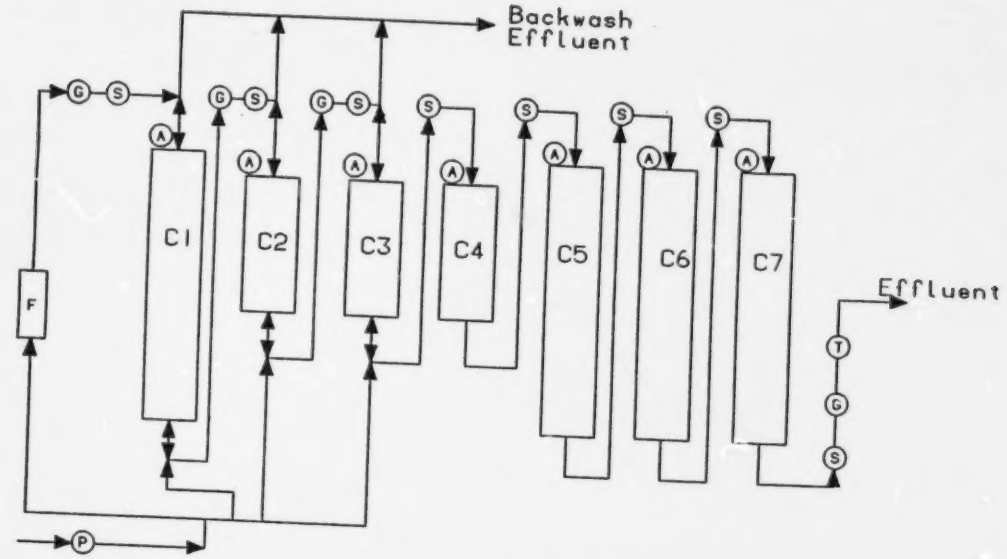
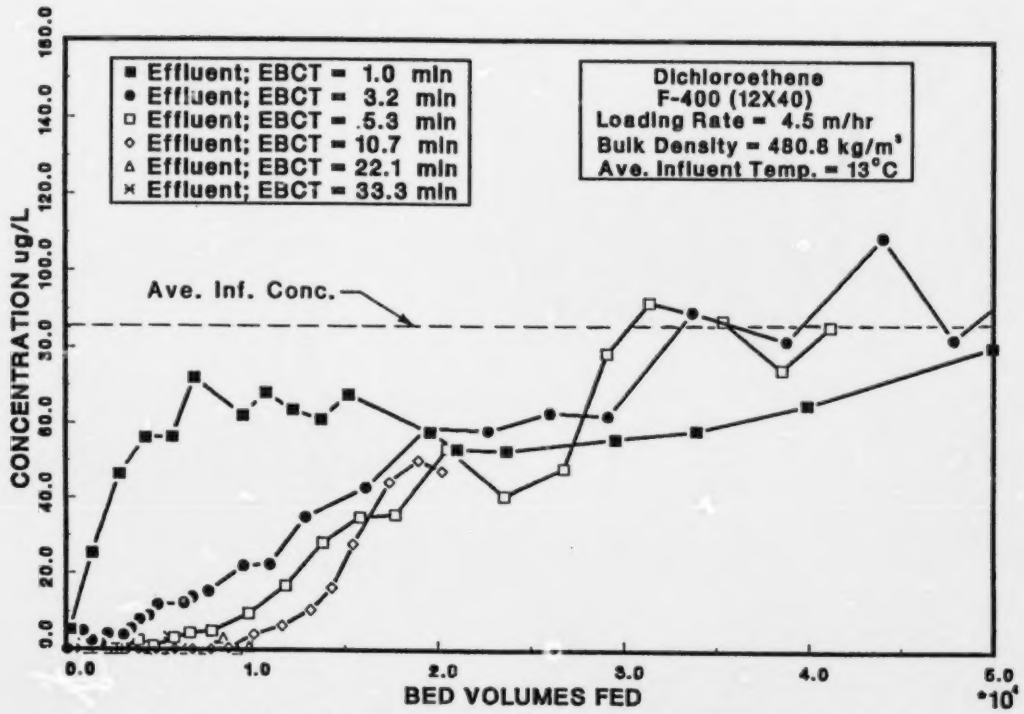
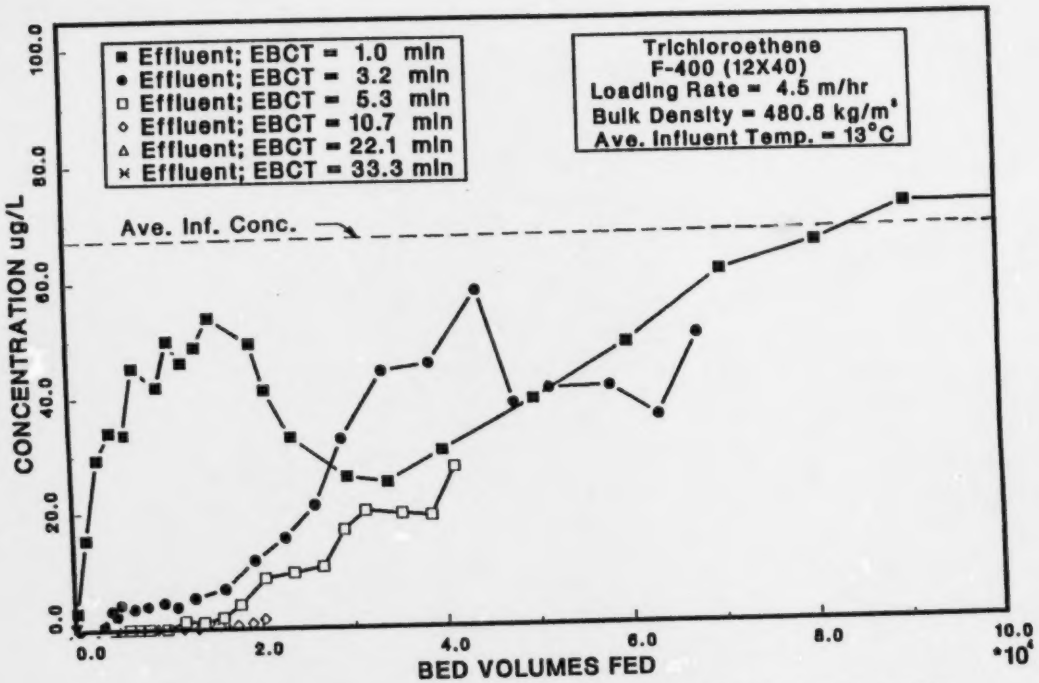


Figure 13. Diagram of the GAC Pilot Plant in Wausau, Wisconsin.



Figures 14. Effluent Concentration of cis 1,2-Dichloroethene for Various Empty Bed Contact Times from the GAC Pilot Plant at Wausau, Wisconsin.



Figures 15. Effluent Concentration of Trichloroethene for Various Empty Bed Contact Times from the GAC Pilot Plant at Wausau, Wisconsin.